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NASA TM-86505

PREPARATION OF SILICON CARBIDE-SILICON
NITRIDE FIBERS BY THE PYROLYSIS OF
POLYCARBOSILAZANE PRECURSORS
(Center Director's Discretionary Fund Final Report)

By B. G. Penn, J. G. Daniels, F. E. Ledbetter, III,
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Space Science Laboratory and
Materials and Processes Laboratory
Science and Engineering Directorate

March 1985



National Aeronautics and
Space Administration

George C. Marshall Space Flight Center



1. REPORT NO. NASA TM-86505		2. GOVERNMENT ACCESSION NO.		3. RECIPIENT'S CATALOG NO.	
4. TITLE AND SUBTITLE Preparation of Silicon Carbide-Silicon Nitride Fibers by the Pyrolysis of Polycarbosilazane Precursors (Center Director's Discretionary Fund Final Report)				5. REPORT DATE March 1985	
				6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) B. G. Penn,* J. G. Daniels,** F. E. Ledbetter, III** and J. M. Clemons**				8. PERFORMING ORGANIZATION REPORT #	
9. PERFORMING ORGANIZATION NAME AND ADDRESS George C. Marshall Space Flight Center Marshall Space Flight Center, Alabama 35812				10. WORK UNIT NO.	
				11. CONTRACT OR GRANT NO.	
				13. TYPE OF REPORT & PERIOD COVERED Technical Memorandum	
12. SPONSORING AGENCY NAME AND ADDRESS National Aeronautics and Space Administration Washington, D.C. 20546				14. SPONSORING AGENCY CODE	
15. SUPPLEMENTARY NOTES *Space Science Laboratory, Science and Engineering. **Materials and Processes Laboratory, Science and Engineering.					
16. ABSTRACT The development of silicon carbide-silicon nitride fibers ($\text{SiC-Si}_3\text{N}_4$) by the pyrolysis of polycarbosilazane precursors that was carried out in this laboratory is reviewed. Precursor resin, which was prepared by heating tris(N-methylamino)-methylsilane or tris(N-methylamino)phenylsilane to about 520°C, was drawn into fibers from the melt and then made unmeltable by humidity conditioning at 100°C and 95 percent relative humidity. The humidity treated precursor fibers were pyrolyzed to ceramic fibers with good mechanical properties and electrical resistivity. For example, $\text{SiC-Si}_3\text{N}_4$ fibers derived from tris(N-methylamino)methylsilane had a tensile rupture modulus of 29×10^6 psi and electrical resistivity of $6.9 \times 10^8 \Omega\text{-cm}$ which is 10^{12} times greater than that obtained for graphite fibers. This research was sponsored by the MSFC Center Director's Discretionary Fund Project [No. 82-13, "Preparation of New Continuous Silicon Carbide-Silicon Nitride ($\text{SiC-Si}_3\text{N}_4$) Fibers by the Controlled Pyrolysis of Organosilane Polymeric Precursors"].					
17. KEY WORDS Silicon Carbide-Silicon Nitride Ceramic Fiber, Silicon Carbide, Silicon Nitride, Polycarbosilazane			18. DISTRIBUTION STATEMENT <i>Benjamin D. Penn</i> Unlimited---Unclassified		
19. SECURITY CLASSIF. (of this report) Unclassified		20. SECURITY CLASSIF. (of this page) Unclassified		21. NO. OF PAGES 11	
				22. PRICE NTIS	

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TECHNICAL MEMORANDUM

PREPARATION OF SILICON CARBIDE-SILICON NITRIDE FIBERS BY THE PYROLYSIS OF POLYCARBOSILAZANE PRECURSORS (Center Director's Discretionary Fund Final Report)

INTRODUCTION

Carbon fibers are widely used in fabricating fiber reinforced composite materials; however, undesirable characteristics such as severe oxidation at temperatures greater than 400°C [1,2], high electrical conductivity which may present a safety hazard during manufacture [3], and poor fiber-matrix adhesion between carbon fibers and thermoplastic or metal matrices [1,2] make the development of alternate reinforcement fibers desirable. Another problem that significantly limits the use of carbon fibers is their reactivity with various metals that are used as matrices in composite materials [2].

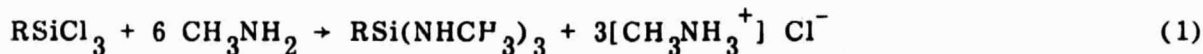
Silicon carbide-silicon nitride ($\text{SiC-Si}_3\text{N}_4$) fibers first developed by Verbeek [4] are an excellent candidate for use in applications that are unsuitable for carbon fibers. These silicon-based ceramic fibers, which are prepared by the pyrolysis of polycarbosilazane precursors, are reported to have good physical and mechanical properties. For example, $\text{SiC-Si}_3\text{N}_4$ fibers derived from tris(N-methylamino)methylsilane are reported to have a tensile strength of 18.8×10^4 psi and elastic modulus of 29×10^6 psi. Moreover, these fibers are stable in air up to 1200°C [4].

This report reviews the work carried out in this laboratory to further develop and characterize $\text{SiC-Si}_3\text{N}_4$ fibers.

MONOMER PREPARATION

The preparation of silicon carbide-silicon nitride fibers consisted of the following steps: preparation of monomeric tris(N-methylamino)alkylsilane, polymerization of the monomer to form a polycarbosilazane precursor, treatment of the precursor to make it unmeltable and pyrolysis of the precursor in an inert environment.

The tri(N-substituted)silanetriamine monomer was prepared by the reaction of a trihalosilane and monomethylamine as shown below:



In this work methyltrichlorosilane or phenyltrichlorosilane was reacted with methylamine to yield tris(N-methylamino)methylsilane or tris(N-methylamino)phenylsilane [5-7]. In the first step of the reaction, the trihalosilane was added dropwise to excess monomethylamine dissolved in petroleum ether or toluene at -40°C. The mixture was then refluxed for 1 hr and the product recovered by distillation. Excess monomethylamine was added for reaction with the HCl generated during the reaction

as shown by equation (1). This is necessary since HCl reacts with SiN bonds [equation (2)] thereby decreasing the monomer yield [8].

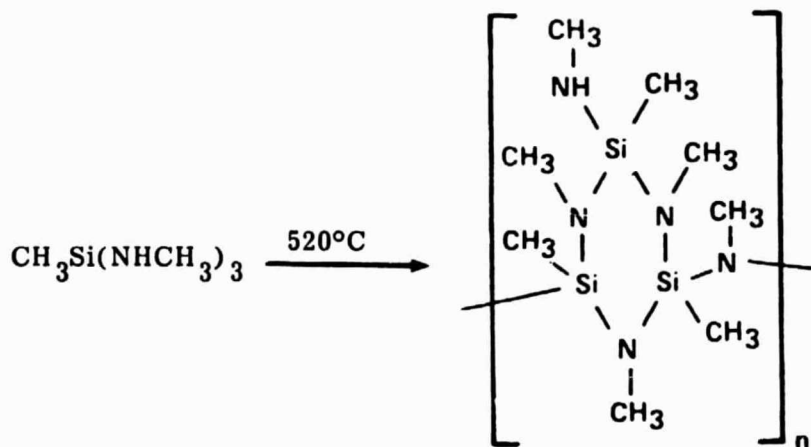


Another precaution was to rigorously exclude water during the reaction since it will cleave the silicon-nitrogen bonds of the monomer.

The monomer, tris(N-methylamino)methylsilane has been prepared by Verbeek [4] and Tansjo [9]. Verbeek prepared the silaneamine by reacting methylamine with methyltrichlorosilane dissolved in petroleum ether at 40°C. Tansjo synthesized the monomer in high yield by the dropwise addition of methyltrichlorosilane to an ice-cooled mixture of excess methylamine dissolved in ether followed by refluxing of the mixture for 1 hr. This procedure resulted in a yield of 71 percent.

POLYMERIZATION OF THE TRI(N-SUBSTITUTED)SILANE TRIAMINE MONOMERS

Tris(N-methylamino)phenylsilane and tris(N-methylamino)methylsilane were used as monomers in the preparation of the polycarbosilazane precursors. This was accomplished by heating the monomers for 1.5 to 4.5 hr in a system that is basically a total reflux distillation system (Fig. 1). The structure shown in equation (1) has been proposed for the polycarbosilazane resulting from the polymerization of tris(N-methylamino)methylsilane [9].



Weight average molecular weights that range from 1533 to 4222 have been obtained by the use of this polymerization technique.

The preparation of a polycarbosilazane by the pyrolysis of tris(N-methylamino)methylsilane has been described by Verbeek [4]. In this method, the liquid monomer which boils at 150°C is conducted for 3 hr through a glass tube that is heated to 520°C, and which is filled with Raschig rings. This mixture is then separated into

the desired carbosilazane resin and redistillable products, which are recycled into the pyrolysis, by heating at 450°C in a cylinder. The molecular weights of the polymers prepared by this method were not reported.

PREPARATION AND CHARACTERIZATION OF POLYCARBOSILAZANE FIBERS

Fibers were drawn from the polycarbosilazane derived from tris(N-methylamino)-methylsilane by touching the surface of the polymer melt with a glass rod and drawing fibers [5]. Lengths up to 6 ft with diameters of 0.5 to 4 mils were obtained using this crude technique. These fibers were made unmeltable by humidity conditioning at 100°C and 95 percent relative humidity for 20 hr. These fibers were found to have tensile strengths of 13,800, 4000 and 1800 psi for diameters of 0.52, 1.74, and 4.97 mil, respectively. This is comparable to the tensile strength value of 1440 psi found for polycarbosilane which is a precursor for SiC fibers [10].

Using the crude fiber drawing technique previously described, fibers were drawn from the polycarbosilazane melt derived from tris(N-methylamino)phenylsilane [6]. A fiber with a diameter of 2.7 mil had a tensile strength of 23,500 psi which is comparable to that reported for the silicon carbide precursor (polycarbosilane) and the polycarbosilazane derived from tris(N-methylamino)phenylsilane (Table 1).

Verbeek has demonstrated that polycarbosilazane resins can be spun into fibers using conventional spinning methods [4]. For example, staple fibers with a cross-section of about 10 to 20 μm were produced by a nozzle blowing process or centrifugal spinning process. In addition, polycarbosilazane resin is reported to be suitable for spinning by conventional dry or wet spinning processes because of its solubility in a large number of organic solvents [4]. The spinning characteristics of the solutions are considerably improved by the addition of auxiliary polymeric material having a molecular weight in excess of 10,000.

The suitability of polycarbosilazane resin for fiber spinning was recently demonstrated by Dunn and Pomplum [11]. These investigators produced fibers by a conventional melt spinning technique using a precursor resin derived from tris(N-methylamino)methylsilane. Polycarbosilazane fibers with diameters of 25 to 30 microns were produced.

PREPARATION AND CHARACTERIZATIONS OF SILICON CARBIDE-SILICON NITRIDE FIBERS

Before pyrolysis to ceramic fibers, the polycarbosilazane precursor fibers were made unmeltable by humidity conditioning at 100°C and 95 percent relative humidity for 20 hr. In addition to this method, Verbeek reported that other pretreatments may be used such as oxidation and/or sulfidation [4]. Suitable reagents for these processes are summarized in Table 2.

After humidity treatment, the hydrolyzed polycarbosilazane fibers were pyrolyzed to SiC-Si₃N₄ fibers at ambient to 1500°C [5]. The pyrolysis process has been

examined using thermogravimetric analysis [12]. Humidity conditioned polycarbosilazane fibers derived from tris(N-methylamino)methylsilane were heated at ambient to 1000°C in a nitrogen atmosphere. As shown in Figure 2, most of the 32.27 percent weight loss occurred at 758° to 808°C. This implies that the precursor fibers should be heated slowly and carefully in this temperature range to decrease flaw formation due to the rapid escape of volatiles.

The stability of silicon carbide-silicon nitride fiber in air at ambient to 1000°C was examined [13]. As shown in Figure 3, the weight loss was insignificant. This was the case after the sample was heated for fifteen minutes under these conditions. Verbeek claims that these fibers have thermal oxidative stability at 1200°C.

The mechanical properties and electrical resistivity of silicon carbide-silicon nitride fibers were found to be good. The tensile strength for SiC-Si₃N₄ fiber derived from tris(N-methylamino)methylsilane was 105×10^3 psi which is comparable to that reported by Verbeek (188×10^3 psi) for the same material [5]. The tensile rupture modulus was found to be 29×10^6 psi and the electrical resistivity was 6.9×10^8 Ω-cm for a 0.6 mil diameter which is 10^{12} times greater than the value reported for graphite fibers.

CONCLUSIONS

The full potential applications of SiC-Si₃N₄ fibers prepared by the pyrolysis of polycarbosilazane precursors cannot be determined without further work; however, data presented here and that of Verbeek [4] indicate that these fibers are an excellent candidate for use as a reinforcement in ceramic, polymer, and metal matrices. For example, the tensile modulus (29×10^6 psi) of silicon carbide-silicon nitride fibers derived from tris(N-methylamino)methylsilane is comparable to other reinforcement fibers and the electrical resistivity value of 6.9×10^8 Ω-cm is 10^{12} times greater than that of graphite. Moreover, these fibers have excellent thermal-oxidative stability as shown by thermogravimetric analysis.

TABLE 1. TENSILE STRENGTHS OF SILICON-BASED
CERAMIC FIBER PRECURSORS

<u>Pyrolyzed Fiber</u>	<u>Precursor [Monomer]</u>	<u>Fiber Diameter (mil)</u>	<u>Tensile Strength (psi)</u>	<u>Reference</u>
SiC-Si ₃ N ₄	Polycarbosilazane [Tris(N-methylamino)methylsilane]	0.52	13,800	5
SiC-Si ₃ N ₄	Polycarbosilazane [Tris(N-methylamino)phenylsilane]	2.7	23,500	6
SiC	Polycarbosilane	—	1,440	10

TABLE 2. PRETREATMENT REAGENTS THAT MAY BE USED TO
MAKE POLYCARBOSILAZANE FIBERS UNMELTABLE [4]

Reagents Suitable for Pretreatment

A. Oxidizing, Dehydrizing, or Dehydrating Agents

1. Air
2. Oxygen
3. Ozone
4. Halogens
5. Nitrogen Oxides
6. Sulfur Vapors
7. Hydrogen Peroxide
8. Organic Peroxides
9. Potassium Permanganate
10. Hydrogen Sulfide
11. Sulfur Dioxide

B. Lewis Acids

1. Aluminum Trichloride
2. Boron Trihalide

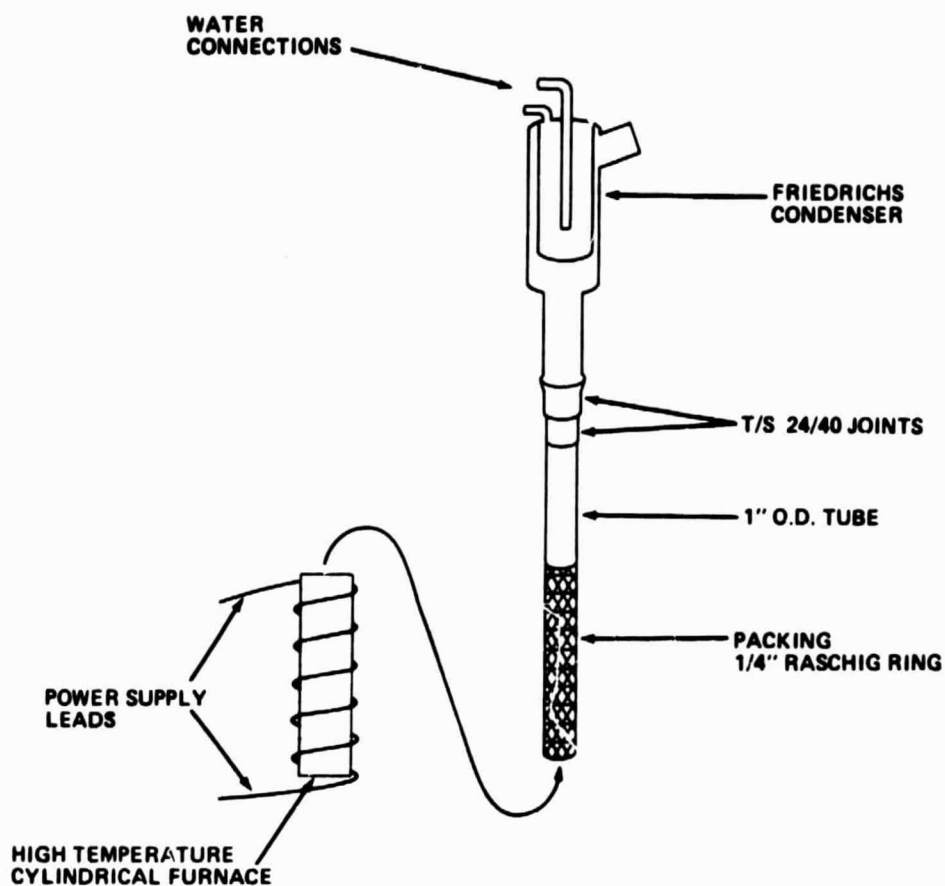


Figure 1. High temperature polymerization system.

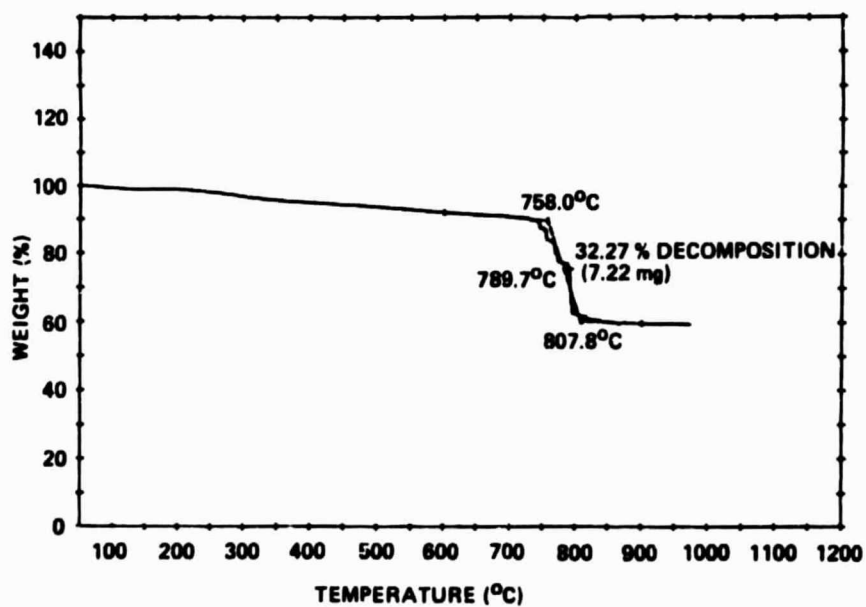


Figure 2. TGA for moisture conditioned polycarbosilazane.

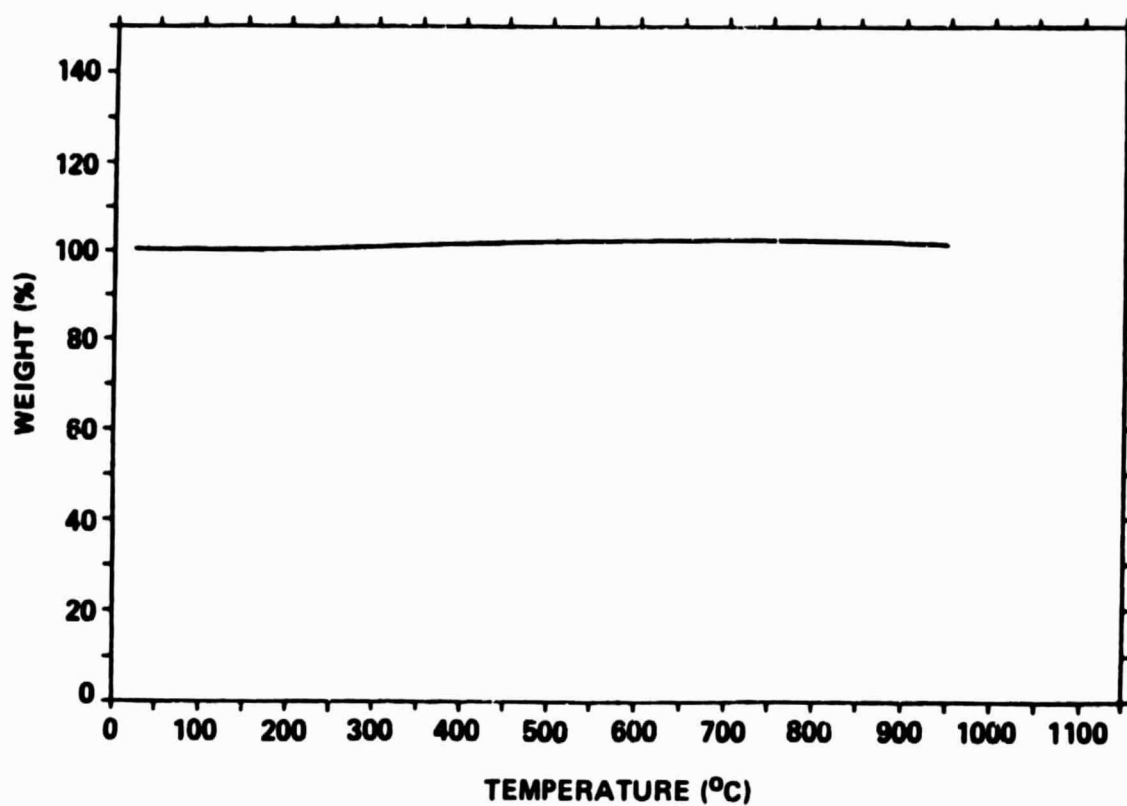


Figure 3. TGA analysis of silicon carbide-silicon nitride fibers (5.63 MG). Heating rate of 10°/min in air.

REFERENCES

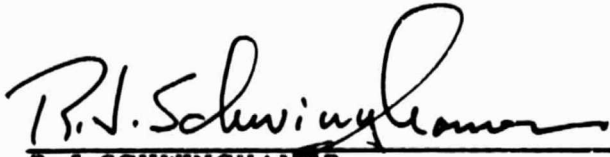
1. Harris, B.: Carbon Fibers in Engineering. Marcus Langley (ed.), McGraw-Hill, New York, 1973, pp. 1-45.
2. Jenkins, G. M. and Kawamura, K.: Polymeric Carbons-Carbon Fibers, Glass, and Char. Cambridge University Press, New York, Chapters 7 and 8, 1976.
3. Cagliostro, D. E.: Textile Research Journal, October 1980, p. 632.
4. Verbeek, W.: Ger. Offen. 2, 218, 960, 1973.
5. Penn, B. G., Ledbetter, F. E. III, Clemons, J. M., and Daniels, J. G.: J. Appl. Polym. Sci., Vol. 27, 1982, p. 3751.
6. Crouse, D. J., Penn, B. G., Ledbetter, F. E. III, Daniels, J. G., and Clemons, J. M.: J. Appl. Polym. Sci. (paper submitted).
7. Penn, B. G., Ledbetter, F. E. III, and Clemons, J. M.: I & EC Process Design and Development, Vol. 23, 1984, p. 217.
8. Fessenden, R. and Fessenden, J.: Chemical Reviews, Vol. 61, 1961, p. 361.
9. Markle, R. A., Sekercioglu, I., Hill, D. L., Wills, R. R., and Sinclair, R. G.: Preparation of $\text{Si}_x\text{N}_y\text{C}_z$ Fibers by the Controlled Pyrolysis of Novel Organosilicon Polymeric Precursors. Battelle Columbus Laboratories Technical Report, Contract No. NAS8-33223, 1980.
10. Andersson, C-H. and Warren, R.: Composites, Vol. 15, No. 1, 1984, p. 16.
11. Pomplum, A. R. and Dunn, S. A.: Bjorksten Research Laboratories, Final Report in Preparation: Development of a Continuous Process for Producing Silicon Carbide-Silicon Nitride Precursor Fibers. Contract No. NAS8-34648, NASA, MSFC, 1985.
12. Ledbetter, F. E. III, Daniels, J. G., Clemons, J. M., Hundley, N. H., and Penn, B. G.: J. Material Science Letters, Vol. 3, 1984, p. 802.
13. Daniels, J. G., Ledbetter, F. E. III, Clemons, J. M., and Penn, B. G.: SAMPE Quarterly, Vol. 15, No. 4, 1984, p. 39.

APPROVAL

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The information in this report has been reviewed for technical content. Review of any information concerning Department of Defense or nuclear energy activities or programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.



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